MAXIMIZING SCIENCE RETURN ON ASTROBIOLOGY AND PLANETARY MISSIONS USING INTEGRATED LIQUID-HANDLING CHEMICAL ANALYSIS SYSTEMS – A STATUS REPORT

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Introduction:

The use of liquids for in situ chemical analysis on planetary missions enables measurements of key organic molecules at parts-per-billion levels in samples that are challenging to analyze using current high-TRL gas phase techniques. This capability becomes particularly valuable when the scientific objective of an in situ chemical analysis involves the search for polar molecules indicative of water-based extant life. These molecules, for example amino acids (building blocks of proteins) and carboxylic acids (constituents of cell membranes), have a very low vapor pressure, and in order to perform a gas phase analysis, one must first perform a sample preparation step in which the molecule is first derivatized to increase its volatility. This process is has been shown to be problematic if the samples contain minerals[1]. Additionally if one wanted to use this type of analysis for a water-based sample, the derivatization agent would preferentially react with the water as well, severely constraining the efficiency of analysis. **An obvious approach to avoid these difficulties in the analysis of liquids is to simply leave them in the liquid state, and use a liquid separation method prior to analysis.** This would be the natural approach to take on an ocean world mission, for example, where ice samples could be acquired by a spacecraft, melted and transferred to an instrument system for direct analysis in that state. The obvious challenge with liquid-based analyses of this kind, of course, is that these systems are low TRL, with little NASA heritage. To that end, our team at JPL has been developing all the necessary "building block" components required for this sort of chemical analysis system (Figure 1) and we are currently in the process of validating a number of different portable automated analyzers that utilize these subsystems, that we have optimized for a range of applications on future missions of exploration (Figures 2 and 3). This contribution will summarize our scientific and technical progress in this area, and highlight the kinds of enhancements to science return on NASA missions that these technologies could provide.

Approach:

The possible pathways for sample flow and analysis we are developing are shown in Figure 1. In all cases, samples (either solid, liquid, or mixtures) are first ingested by the system. For this purpose we have developed a portable subcritical water extraction system (Figure 2) that incorporates elements from a host of previous extraction systems developed at JPL and elsewhere. The liquid output from this extractor is then transferred into a microfluidic based flow injection analysis system (MicroFIA) capable of electrical measurements of pH, conductivity, ORP, and selected ions, as well as performing colorimetric absorbance measurements of ions. To support these measurement capabilities, this system also contains all necessary valving, pumping, and reagent storage capabilities and is battery powered. This system can also act as a "standalone" oceanography sensor for the processing of filtered seawater or lakewater onboard a buoy or underwater explorer.

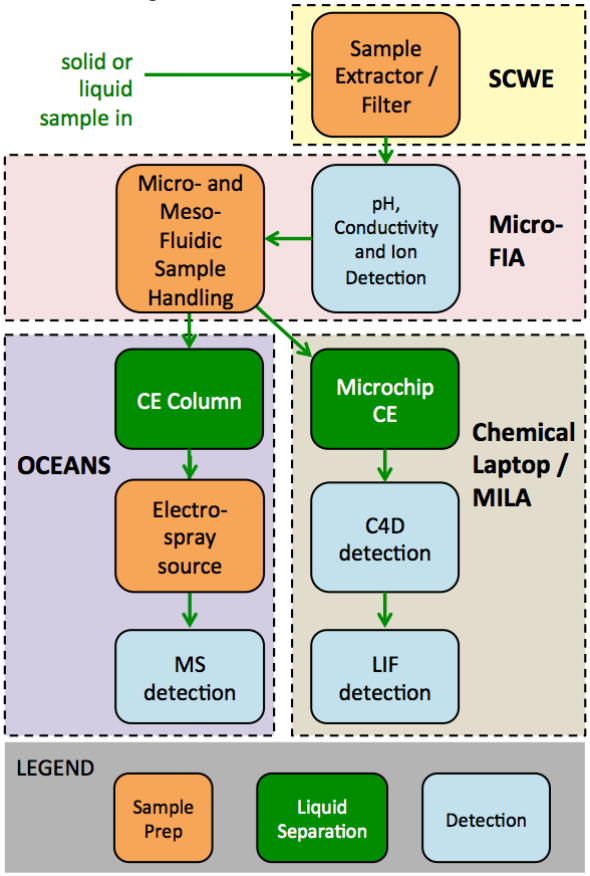

Figure 1. Block diagram displaying sample flow through sample preparation, separation, and detection modules (rounded boxes) under development by our team. We are integrating these modules into complete portable analyzers for use in the field (see Fig 2 and 3).

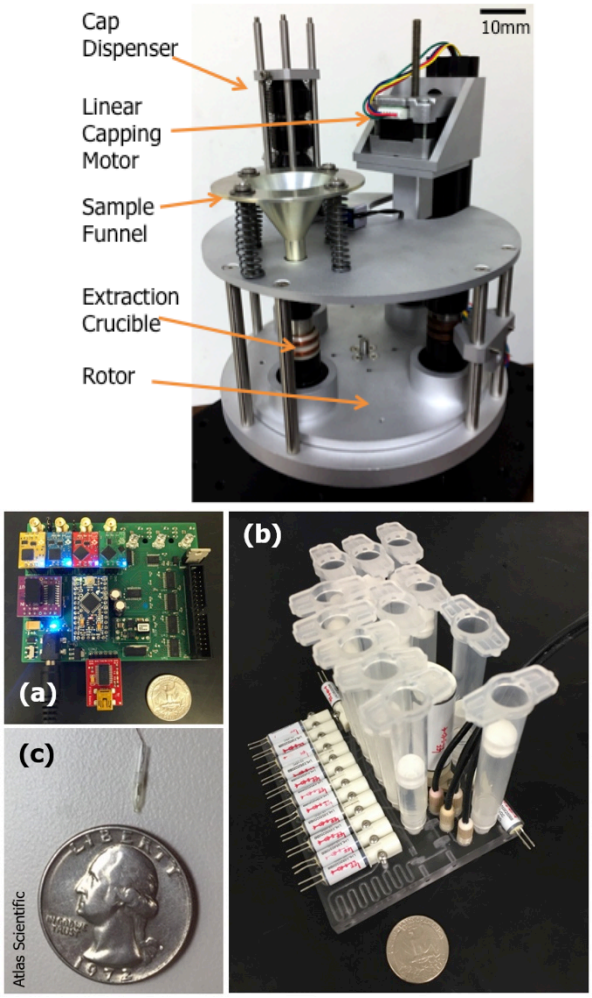

Figure 2. SCWE (*top*) and **MicroFIA** (*bottom* - (a) electronics, (b) assembly, and (c) miniature pH half cell.)

Following initial characterization by the MicroFIA subsystem, liquid samples are separated into their components using electrophoresis, and then detected. Depending upon the form of analysis performed, liquid preparation of these samples must be performed before separation. The bulk of our past efforts have been in the area of microchip electrophoresis coupled to laser-induced fluorescence detection [2]. This requires labeling of samples with a fluorescent dye prior to analysis. We have developed new capillary electrophoresis methods for chiral amino acid analysis that capable of chirally resolving 17 amino acids simultaneously, while still maintaining parts-per-billion detection. The portable system we have validated in the field for performing these analyses is the Chemical Laptop (Figure 3), which we have demonstrated to have an instrumental limit of detection of amino acids of 200pM. We are also currently enhancing this system via the addition of contactless capacitatively coupled conductivity detection (C4D), which, although less sensitive that LIF detection, requires no labeling step and can be used to analyze ions and other inorganic species. Additionally, in partnership with SCIEX we have also recently completed a complete design for a system we dub the Organic Capillary Electrophoresis Analysis System (OCEANS) which couples liquid separations with mass spectrometry detection as well. The design of this system (not yet built) is given in the bottom of Figure 3.

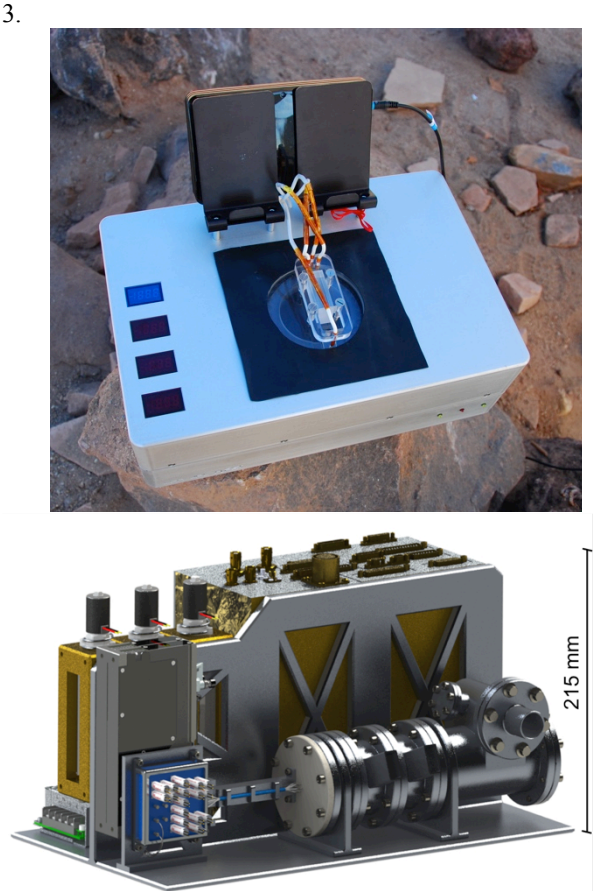

Figure 3. Chemical Laptop (*top* - validated in the field) and the Organic Capillary Electrophoresis Analysis System (**OCEANS**, *bottom* – CAD design of system; key components currently being fabricated, preliminary data acquired).

References:

[1] Stalport F, Glavin DP, Eigenbrode JL, Bish D, Blake D, Coll P, Szopa C, Buch A, McAdam A, Dworkin JP, Mahaffy PR (2012). Planetary and Space Science 67 (1):1-13.

[2] Willis PA, Creamer JS, Mora MF (2015). Analytical and Bioanalytical Chemistry 407 (23):6939-6963.